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Navy Contract Number N6ori-17, T.O. IV
ONR Project Number NR 058 059

Tech. Report No. 9 Project RF-280

THERMAL EXPANSION OF ZIRCONIUM BETWEEN 298° AND 1600° K

by

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TR 280-9

March 16, 1953

Technical Report

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FOREWORD

This work was carried out at The Ohio State University Cryogenic Laboratory under contract with U.S. Navy, Office of Naval Research Contract Number N6ori-17, Task Order IV, ONR Project Number NR 058 039, with The Ohio State University Research Foundation. This report covers information obtained during the study entitled: "High Temperature Thermodynamics of Inorganic Substances." It represents the 9th Technical Report of this series.

Director - H. L. Johnston

Editor - E.R. Fultz

TABLE OF CONTENTS

ABSTRACT

The average coefficients of thermal expansion of hexagonal zirconium between 298° and 1143° K are: 5.5×10^{-6} deg^{-1} along the a-axis, 10.8×10^{-6} deg^{-1} along the c-axis, and 7.2×10^{-6} deg^{-1} for a randomly oriented polycrystalline sample. The average value of the linear coefficient of expansion of cubic zirconium between 1143° and 1600° K is 9.7×10^{-6} deg^{-1}. At the transition there is a decrease in volume of 0.66 percent.

INTRODUCTION

The fact that zirconium crystallizes in the close-packed hexagonal lattice at room temperature and in the body-centered cubic lattice in the temperature range above the transition (at about 1143° K) has been known for some time.[1] Due to the anisotropic crystal structure at lower temperatures, there is some question as to the meaning of measurements reported by Zwikker,[2] by Squire and Kaufmann,[3] and by Adenstedt,[4] of the thermal expansion of bulk samples of zirconium.

In an attempt to clarify these measurements, we have determined the two expansion coefficients of hexagonal zirconium, using the x-ray diffraction method, and have also measured the (isotropic) expansion of cubic zirconium, using the conventional comparator method.

MATERIALS

The zirconium used for these experiments was described in a previous paper.[5] It was prepared by the iodide method, and contained about 1 atom percent hafnium. Specimens for x-ray diffraction were in the form of rods about 0.05 cm diameter. The specimen used for measurements of bulk thermal expansion was about 25.4 cm long and 0.62 cm in diameter, and had two blackbody holes, each 0.099 cm in diameter, drilled 5 cm from each end.

APPARATUS AND PROCEDURE

The x-ray diffraction apparatus described by Edwards, Speiser and Johnston[5] was used. A few modifications were made, the most important being the insertion of a liquid-air trap between the oil diffusion pump and the camera. Nevertheless, it was not possible to obtain, in the apparatus, a vacuum much better than 10^{-5} mm, and considerable trouble was experienced due to contamination of the zirconium specimens. This became most serious at the higher temperatures, so that the x-ray method was not used above 1252° K.

The zirconium rod used for the measurement of the expansion of cubic zirconium was supported inside a 1.26 cm diameter tantalum tube 38.1 cm long, which in turn was supported within an evacuated pyrex tube of about 5 cm diameter. An evenly wound r-f work coil of 0.62 cm copper tubing was placed around the outside of this pyrex tube. The tantalum tube had two small holes, and the pyrex tube two plane windows, opposite the black-body holes in the zirconium rod. Through these openings measurements of temperature were made with a Leeds and Northrup disappearing-filament optical pyrometer, and measurements of position (using the edges of the black-body holes as reference marks) were made with two telescopes mounted on a travelling carriage whose position could be read to within 0.001 mm.

Lattice parameters were calculated from the x-ray diffraction patterns using the method of Cohen,[7] and two corrections were then applied. The first of these corrections was made to account for the impurities (chiefly hafnium) which were initially in the zirconium. On the assumption that the impurities affect both parameters, a_o and c_o, in the same proportion and in the ratio of their concentrations and atomic radii, experimental values were multiplied by a factor of 1.00027 to give the parameters of pure zirconium. The second correction was made to account for the observation that the parameters at room temperatures were usually larger after a high-temperature measurement than before, due to the absorption of impurities (chiefly oxygen and nitrogen gases) by the sample. Half of the increase was subtracted from the measured parameters at high temperature, on the assumption that the impurities were absorbed at a

uniform rate throughout the high-temperature measurement. Experimental data were rejected in a few cases where parameters at room temperature increased by excessive amounts. However, this second correction was not always necessary, since in some of the experiments the specimens were protected from these residual gases by a thin-walled beryllium tube.

EXPERIMENTAL RESULTS

The lattice parameters of pure zirconium at 25° C were found to be $a_o = 3.2265 \pm 0.0010$ kX and $c_o = 5.1371 \pm 0.0015$ kX. The axial ratio c_o/a_o is 1.5922 ± 0.0007. The unit cell volume is 46.314 ± 0.037 kX^3, and the density 6.501 ± 0.005 g/cm^3. The experimental lattice parameters, with cell volumes and expansions for α-zirconium at high temperatures, are listed in Table I.

TABLE I

Thermal Expansion of α-Zirconium

(reference temp = 298.16° K)

T, °K	a_o, kX	c_o, kX	V, kX^3	$\frac{\Delta V}{3V_o} = \frac{\Delta l}{l_o}$
950	3.2393	5.1741	47.019	0.0051
1032	3.2393	5.1751	47.033	.0052
1042	3.2406	5.1816	47.125	.0058
1119	3.2400	5.1803	47.095	.0056
1164	3.2413	5.1856	47.181	.0062

From these data, the average coefficient of linear expansion between 298° and 1143° K is 5.5×10^{-6} deg^{-1} along the a-axis and 10.8×10^{-6} deg^{-1} along the c-axis. The mean coefficient of linear expansion is 7.2×10^{-6} deg^{-1}, being intermediate between the above two values. The assumption of a constant expansion coefficient over the temperature range appears to be justified, within the experimental error, since Squire and Kaufmann[3] obtained

a linear expansion curve by measurement of the gross thermal expansion of a rod over this same range.

The measurement of the lattice parameter of β-zirconium gave $a_o = 3.6089 \pm 0.0020$ kX at 1252° K. The unit cell volume is 47.00 ± 0.08 kX, which gives $\Delta V/V_o = 0.0149$ and $\Delta l/l_o = 0.0050$. Relative to this figure, the values of $\Delta l/l_o$ obtained by direct measurement of thermal expansion are listed in Table II. The density of β-zirconium at 1252° K is 6.406 ± 0.011 g/cm³.

TABLE II

Thermal Expansion of β-Zirconium

T, °K	$\frac{\Delta l}{l_o}$	T, °K	$\frac{\Delta l}{l_o}$
1166	0.0040	1408	0.0066
1251	.0051	1492	.0073
1289	.0053	1533	.0079
1387	.0063	1584	.0080

The $\Delta l/l_o$ values are shown graphically in Fig. 1. The curves obtained by Squire and Kaufmann[3] and Adenstedt[4] fall somewhat lower than ours. Zwikker's[2] curve is lower than ours for α-zirconium but higher for β-zirconium.

ERRORS

We have estimated that the maximum uncertainties in the parameters at room temperature are 0.0010 kX in a_o and 0.0015 kX in c_o. For the high-temperature patterns the corresponding uncertainties are 0.0020 kX and 0.0040 kX, while the uncertainty in a_o for the β-phase is 0.0020 kX. In terms of thermal expansion coefficients, the maximum uncertainty is 10% along the a-axis and 14% along the c-axis.

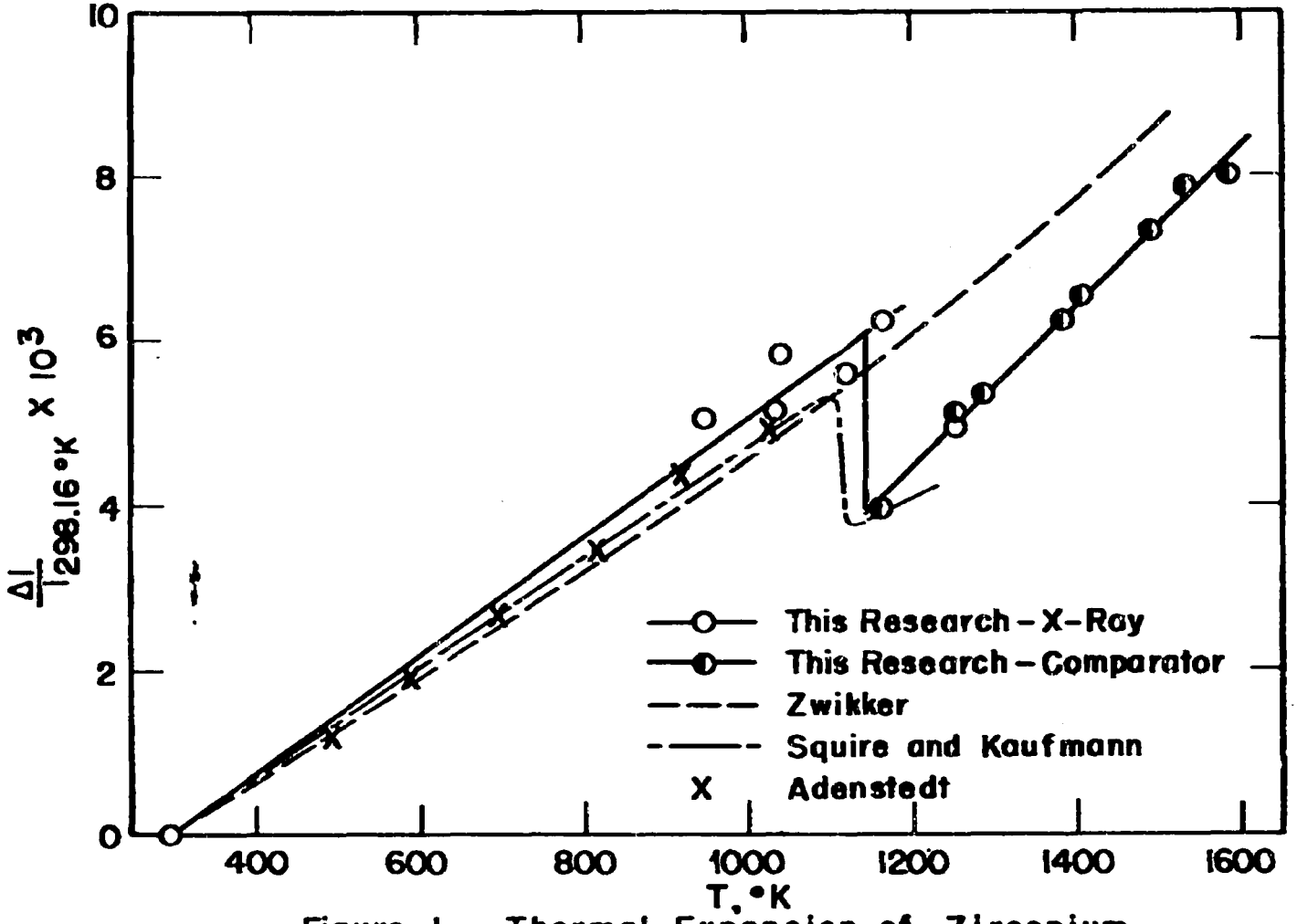

Figure 1 Thermal Expansion of Zirconium

The thermal expansion measurements of β-zirconium with the comparator arrangement were considerably more precise, the maximum uncertainty in the coefficient of expansion, as estimated from the scatter of the experimental points from a straight line, being about 4 %. However, these measurements had to be related to room temperature through the x-ray diffraction measurement of β-zirconium, which could have been in error by as much as 7 %. If this error existed, the whole curve for β-zirconium would be shifted vertically (see Fig. 1).

In view of these comparatively large errors in measuring distances, errors introduced in temperature measurements may safely be neglected.

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